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3. That the attached is, to the best of RWS Group Ltd knowledge and belief, a true translation into the English language of the accompanying copy of the specification filed with the application for a patent Germany on 9 July 1998 under the number 198 30 818.3 and the official certificate attached hereto.
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For and on behalf of RWS Group Ltd

The 25th day of August 2005



FEDERAL REPUBLIC OF GERMANY

Certificate

BASF Aktiengesellschaft

of

Ludwigshafen/Germany

have filed a Patent Application under the title:

"Propoxylate-containing fuel compositions"

on 9 July 1998 at the German Patent and Trademark Office.

The attached document is a correct and accurate reproduction of the original submission for this Patent Application.

The German Patent and Trademark Office has for the time being given the Application the symbol C 10 L 1/18 of the International Patent Classification.

Munich, 9 July 1999

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Propoxylate-containing fuel compositions

The present invention relates to novel propoxylate-containing
5 fuel compositions and novel additive concentrates.

Carburetors and intake systems of gasoline engines as well as injection systems for fuel metering in gasoline and diesel engines are increasingly being contaminated by impurities. The
10 impurities arise from dust particles from the air taken in by the engine, unburnt hydrocarbon residues from the combustion chamber and the vent gases from the crank case which are passed into the carburetor.

15 These residues shift the air/fuel ratio during idling and in the lower part-load range so that the mixture becomes richer and combustion less complete. As a result of this, the proportion of uncombusted or partially combusted hydrocarbons in the exhaust gas increases and the gasoline consumption rises.

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It is known that these disadvantages are avoided by using fuel additives for keeping valves and carburetor or injection systems clean (cf. for example: M. Rossenbeck in Katalysatoren, Tenside, Mineralöladditive, editors J. Falbe, U. Hasserodt, page 223,
25 G. Thieme Verlag, Stuttgart 1978). A distinction is now made between two generations, depending on the mode of action and preferred place of action of such detergent additives. The first generation of additives could only prevent the formation of deposits in the intake system but could not remove existing
30 deposits. On the other hand, the additives of the second generation can prevent and eliminate deposits (keep-clean and clean-up effect). This is permitted in particular by their excellent heat stability in zones of high temperature, in particular at the intake valves.

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The molecular structural principle of these additives of the second generation which act as detergents is based on the linking of polar structures with generally higher molecular weight nonpolar or oleophilic radicals.

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Typical members of the second generation of additives are products based on polyisobutene in the nonpolar molecular moiety, in particular additives of the polyisobutylamine type. Such detergents can be prepared by two different multistage synthesis
45 processes, starting from polyisobutenes: the first process takes place via chlorination of the polymeric parent structure, followed by nucleophilic substitution of the polymeric parent

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structure by amines or preferably ammonia. The disadvantage of this process is the use of chlorine, which results in the occurrence of chlorine- or chloride-containing products, which is now by no means desirable. In the second process, the polyiso-
5 butylamines are prepared starting from polyisobutene, by hydroformylation and subsequent reductive amination according to EP-A-0 244 616.

Detergent additives, which may originate from a large number of
10 chemical classes of substances, are used in general in combination with a carrier oil. The carrier oils have an additional "washing function", often support and promote the detergents in their action and can help to reduce the required amount of detergent. Specific detergents do not display their
15 action at all until they are combined with a carrier liquid. Usually, viscous, high-boiling and in particular heat-stable liquids are used as carrier oils. they coat the hot metal surface (for example the intake valve) with a thin liquid film and thus prevent or delay to a certain degree the formation or deposition
20 of decomposition products on the metal surfaces, but without being able to replace the detergent additive components.

Suitable carrier oils for the fuels for internal combustion engines are, for example, high-boiling refined mineral oil
25 fractions, as well as synthetic liquids. Suitable mineral carrier oils are, for example, fractions obtained in mineral oil processing.

Examples of suitable synthetic carrier oils are polyolefins,
30 (poly)esters, (poly)alkoxylates, and in particular aliphatic polyethers, aliphatic polyetheramines, alkylphenol-initiated polyethers and alkylphenol-initiated polyetheramines.

Adducts of butylene oxide with alcohols have excellent solubility
35 in fuels but are comparatively expensive products and the starting material butylene oxide has to be prepared by a relatively expensive procedure.

More economical carrier oils can be made available in the form of
40 adducts of propylene oxide with alcohols.

EP-A-0 704 519 describes propoxylates as carrier oil components in combination with a high molecular weight amine and a hydrocarbon polymer.

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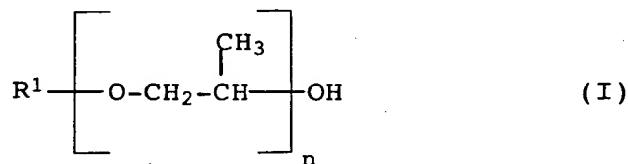
EP-A-0 374 461 describes such propoxylates for use as a carrier oil in combination with esters of mono- or polycarboxylic acids and alcohols or polyols and amino- or amido-containing detergents. EP-A-0 374 461 expressly states (cf. page 4, line 29 et seq.) that the sole use of the propoxylates described therein reduces the intake valve deposits only to an insufficient extent, namely to values of from 80 to 220 mg per valve.

However, the known additive systems of the prior art which contain carrier oils based on propylene oxide still do not have the optimum cleaning effect in the engine. Furthermore, such adducts of propylene oxide with alcohols often give rise to problems owing to their limited solubility in fuels and owing to their poor compatibility with other additives, so that separation may occur. This effect is displayed in a particularly dramatic way when additive concentrates - additive systems are usually marketed as such - are to be formulated.

It is an object of the present invention to provide novel fuel compositions having improved properties for internal combustion engines. In particular, the novel fuel compositions should lead to substantially reduced intake valve deposits.

We have found, surprisingly, that this object is achieved by the provision of a fuel composition for internal combustion engines, comprising a principal amount of a liquid hydrocarbon fuel and an amount, which has a cleaning effect, in particular reduces intake valve deposits, of at least one propoxylate additive of the formula I

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where

n is an integer from 10 to 20 and

R¹ is straight-chain or branched C₈-C₁₈-alkyl or C₈-C₁₈-alkenyl, preferably C₈-C₁₈-alkyl.

The novel fuel compositions have the surprising advantage that they reduce deposits in the region of the intake valves substantially better than the corresponding shorter-chain or

longer-chain propoxylates. This is surprising in particular because it has been assumed to date that compounds of the type used are suitable only as carrier oils for fuel compositions but carrier oils per se do not have a satisfactory cleaning effect in
5 the intake system.

To achieve the effect shown according to the invention, the propoxylates of the above formula I should be used in an amount of from about 50 to 5000, preferably from about 100 to 2500, in
10 particular from about 300 to 1000, mg/kg of fuel.

The above object according to the invention is furthermore achieved by providing fuel compositions for internal combustion engines which contain a principal amount of a liquid hydrocarbon
15 fuel and an amount, which has a cleaning effect and substantially reduces impurities in the intake system, of an additive combination comprising:

- a) at least one propoxylate additive, preferably an alkanol
20 propoxylate, of the above formula I and
- b) at least one polyalkylamine of a formula II



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where

R^2 is a straight-chain or branched polyalkyl radical having a number average molecular weight of from about 500 to
30 5000.

The novel fuel compositions which contain the abovementioned additive combination also surprisingly substantially reduce intake valve deposits.

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In the fuel compositions according to the second embodiment described above, the additives of the formula I and the additives of the formula II together are present in a total amount of from about 100 to 10,000, preferably from about 300 to 5000, in
40 particular from about 500 to 3000, mg/kg of fuel. The additives of the formula I and those of the formula II are present in a molar ratio of from about 1:10 to 10:1, for example from about 1:5 to about 5:1, in particular from about 1:2 to 2:1.

45 C_8 - C_{18} -Alkyl radicals which may be used according to the invention are straight-chain or branched, saturated carbon chains of 8 to 18 carbon atoms. For example, the following radicals may be

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mentioned: n-hexyl, 1-, 2- or 3-methylpentyl, straight-chain heptyl, octyl, nonyl, decyl, undecyl, dodecyl, tridecyl, tetradecyl, pentadecyl, hexadecyl, heptadecyl and octadecyl and the singly or multiply branched analogs thereof. Preferred

- 5 long-chain radicals are branched or straight-chain C_{10} - C_{16} -alkyl, in particular C_{12} - C_{14} -alkyl. Tridecyl radicals are especially preferred.

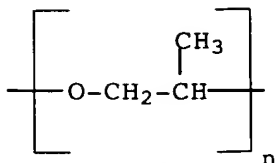
- C_8 - C_{18} -Alkenyl radicals which can be used according to the
10 invention are straight-chain or branched carbon chains having at least one carbon-carbon double bond and 8 to 18 carbon atoms. Examples of monounsaturated C_8 - C_{18} -alkenyl radicals are radicals such as straight-chain octenyl, nonenyl, decenyl, undecenyl, dodecenyl, tridecenyl, pentadecenyl, hexadecenyl, heptadecenyl
15 and octadecenyl and the branched analogs thereof, it being possible for the double bond to occur in any desired position. Also included according to the invention are both the cis- and the trans-isomers of the above C_8 - C_{18} -alkenyl radicals. Preferred monounsaturated long-chain radicals are the C_{10} - C_{16} -alkenyl
20 radicals.

- Polyalkyl radicals which may be used according to the invention are preferably obtainable by homo- or copolymerization of the straight-chain or branched C_2 - C_{30} -alkenes, C_2 - C_6 -alkenes and in
25 particular C_2 - C_4 -alkenes being preferred. Particularly preferred C_2 - C_4 -alkenes are 1-alkenes, such as propylene, 1-butene and isobutene. The number average molecular weight of such polyalkyl radicals is roughly in the range from 500 to 5000, preferably from about 800 to 1500, in particular about 1000. For example,
30 the polyalkyl radical may be derived from a copolymer of 1-butene and isobutene, and, for example, have a number average molecular weight of from about 800 to about 1500.

- Propoxylates of the formula I which are particularly preferred
35 according to the invention are compounds in which R^1 is straight-chain or branched alkyl of 10 to 16 carbon atoms, or mixtures thereof. Particularly preferred propoxylates of the formula I are those in which the radical R^1 is alkyl of 12 to 14 carbon atoms or is a mixture of such alkyl radicals. A propoxylate of the formula
40 I in which the radical R^1 has 13 carbon atoms is particularly preferred.

- A further group of propoxylates preferred according to the invention comprises those composed of from 12 to 18 repeating
45 units, in particular from 14 to 17 and especially from 14 to 16 repeating units, of the formula

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The most preferred class of propoxylates comprises those having
10 15 repeating propoxylate units. It must be borne in mind that the
above numerical data for n may also be average values since many
of the known preparation methods for such adducts of alkylene
oxides with alcohols usually lead to a product mixture with
varying molecular weight distribution.

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Alkoxyates of the formula I which are most preferred according
to the invention are adducts of from 14 to 16, in particular 15,
propylene oxide units of the above formula with a branched
C₁₃-alcohol, in particular C₁₃-monoalcohol. Branched C₁₃-alcohols
20 which may be used according to the invention are, for example,
also obtainable by oligomerization of C₂-C₆-olefins, in particular
C₃- or C₄-olefins, and subsequent hydroformylation. A reaction
mixture which may be obtained thereby and which may comprise, for
example, different alcohol isomers can be used directly for the
25 preparation of the additive components used according to the
invention. However, prior separation of the reaction mixture can,
if required, also be carried out.

The preferred alkanol propoxylates according to the invention are
30 prepared in the conventional manner by reacting an alcohol, as an
initiator molecule, with propylene oxide in the presence of an
alkali, e.g. sodium hydroxide solution, potassium hydroxide
solution, sodium methylate, potassium methylate or another alkali
metal alkoxide, at from about 120 to 160°C, preferably from about
35 130 to 160°C, to give the desired adducts. After alkoxylation is
complete, the propoxylate is freed from the catalyst, for example
by treatment with magnesium silicate. The preparation is thus
carried out analogously to the phenol-initiated alkoxyates
described in DE-A-41 42 241.

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The polyalkylamines of the formula II are compounds known per se
and can be prepared by hydroformylation of reactive polyalkenes
and subsequent reductive amination of the oxo product. The
reactive polyalkenes having an average molecular weight of from
45 about 500 to 5000, are homo- or copolymers of straight-chain or
branched C₂-C₃₀-alkenes, preferably C₂-C₆-alkenes, in particular
C₂-C₄-alkenes. Reactive polyalkenes comprise unsaturated polymers

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of high chemical homogeneity, more than 10% of the double bonds being in the alpha position. One possibility for the preparation of reactive polyalkenes is disclosed in DE-A-27 02 604.

Particularly preferred reactive polyalkenes are those which are
5 prepared from 1-alkenes, in particular propylene, 1-butene, isobutene or mixtures thereof.

Suitable polyalkylamines of the formula II are also amines according to EP-A-0 244 616 and EP-A-0 695 338, the content of
10 which is hereby expressly incorporated by reference.

EP-A-0 244 616 describes in particular those polyalkylamines in which R^2 is derived from isobutene and up to 20% by weight of n-butene. EP-A-0 695 338 describes in particular those polyalkylamines in which R^2 is derived from one or more 1-n-alkenes of
15 3 - 6 carbon atoms and up to 50% by weight of ethene.

Novel fuel compositions comprise both diesel fuels and fuels for gasoline engines. Suitable fuels for gasoline engines are leaded and in particular unleaded regular and premium grade gasoline.

20 The gasolines may also contain components other than hydrocarbons, for example alcohols for [sic] methanol, ethanol and tert-butanol, and ethers, e.g. methyl tert-butyl ether. In addition to the additives of the above formula I and, if required, II, the novel fuel compositions may contain further
25 additive components.

Further additives which may be used according to the invention are described, for example, in European Patent Applications EP-A-0 277 345, 0 356 725, 0 476 485, 0 484 736, 0 539 821,
30 0 543 225, 0 548 617, 0 561 214, 0 567 810 and 0 568 873; in German Patent Applications DE-A-39 42 860, 43 09 074, 43 09 271, 43 13 088, 44 12 489, 44 25 834, 195 25 938, 196 06 845, 196 06 846, 196 15 404, 196 06 844, 196 16 569, 196 18 270 and 196 14 349; and in WO-A-96/03479.

35 Particularly useful liquid detergent additives are sold by BASF AG, Ludwigshafen, under the tradename Kerocom® PIBA. These contain polyisobutenamines dissolved in aliphatic C_{10-14} -hydrocarbons.

40 In addition to the above additives, further conventional fuel additives may be present, for example corrosion inhibitors, demulsifiers, stabilizers, antioxidants and dyes.

45 Corrosion inhibitors are generally ammonium salts of organic carboxylic acids which, by virtue of the starting compound having the appropriate structure, tend to form films. Amines for

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reducing the pH are also frequently used in corrosion inhibitors. Heterocyclic aromatics are generally used as corrosion inhibitors for nonferrous metals.

5 Examples of antioxidants or stabilizers are in particular amines, such as para-phenylenediamine, dicyclohexylamine, morpholine or derivatives of these amines. Phenolic antioxidants, such as 2,4-di-tert-butylphenol or 3,5-di-tert-butyl-4-hydroxyphenyl-propionic acid and derivatives thereof, are also added to fuels.

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The demulsifiers used are usually salts of fatty acids and sulfonic acids.

If required, carrier oils may furthermore be added, the carrier
15 oils differing from the compounds of the formula I.

Examples of useful carrier oils or carrier liquids are mineral carrier oils, synthetic carrier oils and mixtures thereof which are compatible with the above additive or additives and with the
20 fuel. Suitable mineral carrier oils are fractions obtained in mineral oil processing, such as kerosene or naphtha, brightstock or mineral oils having a viscosity of SN 500 - 900, as well as aromatic hydrocarbons, paraffinic hydrocarbons and alkoxyalkanols.

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Examples of suitable synthetic carrier oils are polyolefins, (poly)esters, (poly)alkoxylates, and in particular aliphatic polyethers, aliphatic polyetheramines, alkylphenol-initiated polyethers and alkylphenol-initiated polyetheramines. Suitable
30 carrier oil systems are described, for example, in DE-A-38 38 918, DE-A-38 26 608, DE-A-41 42 241, DE-43 09 074, US-A-4 877 416 and EP-A-0 452 328. Examples of particularly suitable synthetic carrier oils are alcohol-initiated polyethers having from about 20 to 25 C₃-C₆-alkylene oxide units, for example
35 selected from propylene oxide units, n-butylene oxide units and isobutylene oxide units or mixtures thereof.

The present invention furthermore relates to fuel additive mixtures which are preferably present in the form of additive
40 concentrates and, as intake valve cleaner components, contain at least one propoxylate additive of the formula I according to the above definition, in particular an alkanol propoxylate of the above formula I, if required in combination with at least one polyalkylamine of the formula II according to the above
45 definition and, if required, at least one further other fuel additive. According to a preferred embodiment, the novel fuel

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additive mixtures contain propoxylate and polyalkylamine in a molar ratio stated above for the novel fuel compositions.

The present invention furthermore relates to the use of at least
5 one propoxylate of the above formula I, if required in combination with at least one polyalkylamine of the above formula II, as an intake valve cleaner additive for fuel compositions for internal combustion engines.

10 The examples which follow illustrate the invention in more detail.

Examples

15 Example 1: Engine test for testing the action as intake system cleaner

The engine tests were carried out in a 1.2 l Opel Kadett engine according to CEC F/04/A/87. Fuel used: unleaded European premium
20 grade.

The additives used were prepared by the following general method.

A dewatered mixture of the alcohol used as initiator and KOH is
25 initially taken in a pressure-resistant vessel, the amount of KOH used being from about 0.01 to 1, preferably from 0.05 to 0.5, % by weight of the expected total weight of the reaction product. The apparatus is then flushed several times with nitrogen and is heated to about 135°C and the propylene oxide is then metered in
30 while stirring at a constant temperature and at a pressure of from 3 to 30 bar via a dip tube or onto the surface. After metering is complete, the reaction mixture is further stirred until the pressure remains constant. After the reactor content has been cooled to about 50°C, the reaction vessel is let down and
35 is flushed with nitrogen. The product is freed from volatile components, advantageously under reduced pressure, and, if necessary, clarified by filtration. Before the filtration, it is advantageously removed from the catalyst by methods known to a person skilled in the art, for example treatment with ion
40 exchanger, precipitation or absorption, etc.

Table 1

5	Additive	Dose [mg/kg]	Intake valve deposits [mg] ¹⁾				
			Valves	1	2	3	4
10	Tridecanol x 10 Propylene oxide	400		13 (277)	2 (175)	11 (183)	58 (337)
	Tridecanol x 15 Propylene oxide	400		4 (277)	0 (175)	1 (183)	0 (337)
	Tridecanol x 20 Propylene oxide	400		17 (277)	0 (175)	0 (183)	22 (337)
	Tridecanol x 25 Propylene oxide	400		144 (514)	34 (303)	305 (300)	41 (519)
15	Tridecanol x 30 Propylene oxide	400		160 (514)	2 (303)	28 (300)	86 (519)

1) Values in brackets: Deposits without addition of additives; the different values are due to differences in the unleaded European premium grade used

Example 2: Cooperation of tridecanol propoxylate and polyisobutenamine

The following test results (engine: Mercedes Benz M 102 E) show that a maximum effect is also achieved with a tridecanol propoxylate with 15 mol of propylene oxide. In a polyisobutenamine-containing fuel additive package (PIBA content 25% by weight) the carrier oil component was varied in the manner stated.

Table 2

35	Additive	Dose* [mg/kg]	Intake valve deposits [mg]*				
			Valve	1	2	3	4
	Starting value	-		283	132	232	290
40	Tridecanol x 15 propylene oxide	500		7	10	89	19
	Tridecanol x 25 propylene oxide	500		59	97	39	40

* Dose of a formulation comprising propoxylate and PIBA in a weight ratio of about 1:1; total amount of PIBA + propoxylate in the formulation is 50% by weight.

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Example 3: Compatibility investigation

The following test results show that a tridecanol propoxylate with 15 mol of propylene oxide has optimum compatibility with the 5 components of an additive package (concentrate).

In a polyisobutenamine-containing fuel additive package, the carrier oil component was replaced with the novel tridecanol propoxylate with 15 mol of propylene oxide or with a 10 corresponding propoxylate not according to the invention and comprising 25 mol of propylene oxide. The formulations [sic] with the novel component was homogeneous whereas phase separation occurred in the comparative formulation when left to stand at 20°C.

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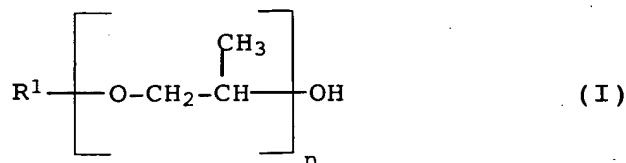
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We claim:

1. A fuel composition for internal combustion engines,
comprising a principal amount of a liquid hydrocarbon fuel
and an amount, which has a cleaning effect, of at least one
propoxylate additive of the formula I



where

n is an integer from 10 to 20 and

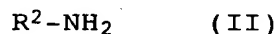
R¹ is straight-chain or branched C₈-C₁₈-alkyl or
C₈-C₁₈-alkenyl.

2. A fuel composition as claimed in claim 1, which contains the
propoxylate of the formula I in an amount of from about 50 to
5000 mg/kg of fuel.

3. A fuel composition for internal combustion engines,
containing a principal amount of a liquid hydrocarbon fuel,
comprising an amount, which has a cleaning effect, of an
additive combination comprising

a) at least one propoxylate additive of the formula I as
claimed in claim 1; and

b) at least one polyalkylamine additive of the formula II



where

R² is a straight-chain or branched polyalkyl radical
having a number average molecular weight of from about
500 to about 5000.

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4. A fuel composition as claimed in claim 3, which contains the additives of the formula I and of the formula II in a total amount of from about 100 to 10,000 mg/kg of fuel.
- 5 5. A fuel composition as claimed in claim 3 or 4, which contains the additives of the formula I and of the formula II in a molar ratio of from about 1:10 to about 10:1.
- 10 6. A fuel composition as claimed in any of claims 3 to 5, comprising at least one polyalkylamine additive of the formula II, where R^2 is a radical derived from identical or different C_2 - C_{30} -alkenes.
- 15 7. A fuel composition as claimed in any of claims 3 to 6, which contains, as an additive of the formula II, at least one polyisobutenamine having a number average molecular weight of from 800 to 1500.
- 20 8. A fuel composition as claimed in any of the preceding claims, which comprises at least one additive of the formula I, where n is the integer of 15 and R^1 is straight-chain or branched C_{13} -alkyl.
- 25 9. A fuel additive mixture which contains, as intake valve cleaner component, at least one propoxylate according to the definition in claim 1, if required in combination with at least one polyalkylamine according to the definition in claim 3 and, if required, together with further conventional fuel additives.
- 30 10. A fuel additive mixture as claimed in claim 9, which contains propoxylate and polyalkylamine in a molar ratio of from about 1:10 to 10:1.
- 35 11. The use of at least one propoxylate according to the definition in claim 1, if required in combination with at least one polyalkylamine according to the definition in claim 3, as an intake valve cleaner additive for fuel compositions for internal combustion engines.

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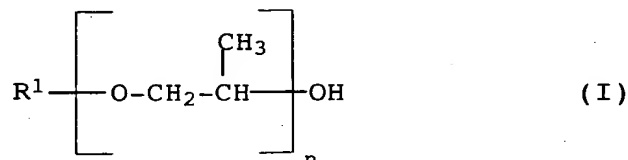
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Abstract

Fuel compositions for internal combustion engines, comprising a
5 principal amount of a liquid hydrocarbon fuel and an amount,
which has a cleaning effect, of at least one propoxylate additive
of the formula I

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where

n is an integer from 10 to 20 and

20 R^1 is straight-chain or branched C_8 - C_{18} -alkyl or C_8 - C_{18} -alkenyl,

if required in combination with at least one polyalkylamine
additive of the formula II

25



where

30 R^2 is a straight-chain or branched polyalkyl radical having a
number average molecular weight of from about 500 to about
5000,

and fuel additive compositions which contain propoxylates of the
formula I and, if required, polyalkylamines of the formula II as
35 intake valve cleaners.

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